Isotope effects on the picosecond time-resolved emission spectroscopy of tris(2,2 '-bipyridine)ruthenium (II)

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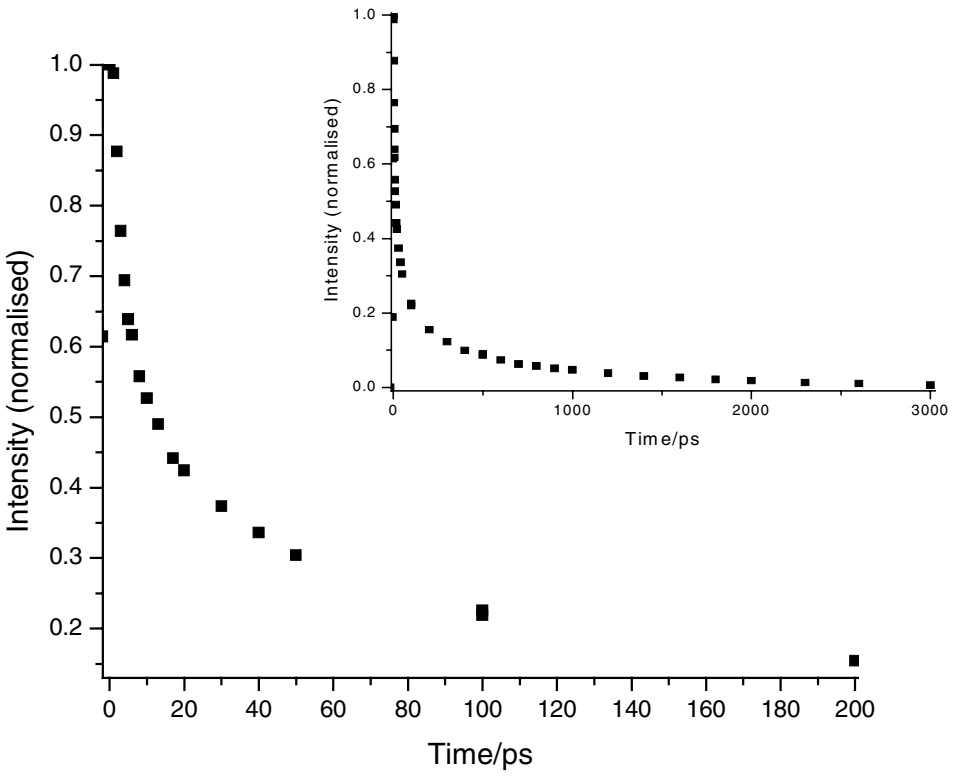
Supporting information.

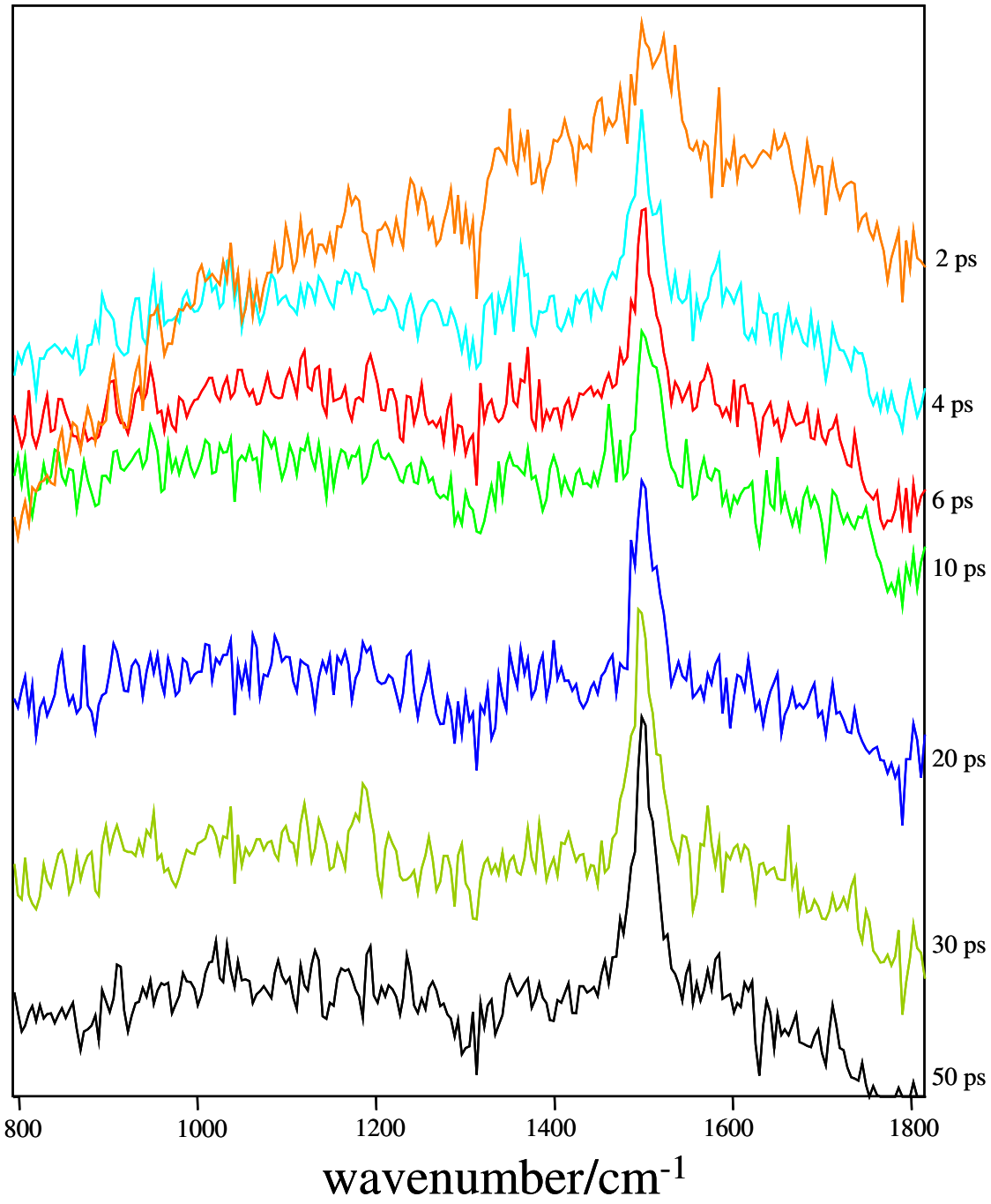
Experimental section. Chemicals. $RuCl_3.xH_2O$ (Avacado), 2,2'-bipyridine (Aldrich) and $[Ru([H_8]\text{-bpy})_3]Cl_2.2H_2O$ (Aldrich) were used as received without further purification. All solvents used were of spectroscopic grade. $[D_8]$-2,2'-bipyridine, $[D_{14}]$-5,6-$[H_2]$-4,7-diphenyl-1,10-phenathroline, (*see* Keyes et al. *J. Chem. Soc. Dalton Trans*., **1995**, 2705. Browne et al. Vos, J.G., *Inorg. Chem.,* **2002**, *41*, 4245.) $[Ru([H_8]\text{-bpy})_3]Cl_2$, $[Ru([H_8]\text{-bpy})_3](PF_6)_2$, $[Ru([D_8]\text{-bpy})_3]Cl_2$, $[Ru([D_8]\text{-bpy})_3](PF_6)_2$, $[Ru([H_{16}]\text{-ph}_2\text{phen})_3]Cl_2$ and $[Ru([D_{14}]\text{-ph}_2\text{phen})_3]Cl_2$ were prepared by literature procedures. (*See* Belser et al. *Helv. Chimica Acta*, **1980**, *63*, 1675. Klassen, D.M. *Inorg. Chem*., **1976**, *15*, 3166. Kakoti et al.. *Inorg. Chem*., **1992**, *31*, 1302. Strouse et al. *Inorg. Chem*., **1992**, *31*, 3004. Fletcher et al. S. *J. Chem. Soc., Dalton Trans*., **2001**, 2641.)

The experiments were carried out using a Ti:sapphire based regenerative amplifier generating 2-3 mJ pulses at 820 nm with a ~ 1 ps pulse duration at 1 kHz repetition rate. About 500 µJ of the fundamental pulse energy was used to drive a 4 ps optical Kerr gate incorporated in the Raman/fluorescence collection system. (*see* Towrie et al. *Meas. Sci. Technol.* **1998**, *9*, 816. Matousek et al. *J. Raman Spectrosc*., **2001**, *32*, 983.) The emitted light was dispersed in a single stage spectrometer using a 100 groves/mm grating and detected with a nitrogen cooled, back illuminated CCD camera. A small part of the fundamental pulse was frequency doubled to provide 5 -10 µJ at 410 nm and then sent onto a computer controlled optical delay line before incident on the sample. The excitation beam was focused to ~ 100 µm into a vertically flowing open jet of 500 µm diameter. The fluorescence measurement was performed at the magic angle to eliminate the effect of sample reorientation. The Kerr gate was opened to sample fluorescence spectrum at various time delays following excitation pulse. All TRF spectra were obtained by subtracting the negative the negative time delay signal from the positive time delay signal. The sample concentration was typically 1-5 mM. The time resolved spectra are not corrected for the detection system transmission/sensitivity variation with wavelength. In the time resolved luminescence spectra (table of contents graphic and Figure 1) Note the transient spectra are uncorrected for spectrometer throughput and the apparent vibrational progression observed in the 520 nm emission is due to the holographic filter employed.

S1 Normalized luminescence decay trace of $[Ru([D_8]\text{-bpy})_3]^{2+}$ in H_2O between 0 and 210 ps. λ_{exc} 410 nm, λ_{em} 510 to 545 nm (inset 0 to 3000 ps)



S2. Time resolved resonance Raman spectra of $[Ru([H8]\text{-}bpy)_3]^{2+}$ in H_2O between 2 and 50 ps following excitation. Steady state spectra have been subtracted. Pump = 410 nm; probe = 470 nm. Spectra offset on the vertical axis for clarity.



S3. Time resolved resonance Raman spectra of $[Ru([D_8]\text{-bpy})_3]^{2+}$ between 0 and 50 ps following excitation in H_2O. Steady state spectra have been subtracted. Pump = 410 nm; probe = 470 nm. Spectra offset on the vertical axis for clarity.